(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
15 February 2001 (15.02.2001)

PCT

(10) International Publication Number
WO 01/10963 A1

(51) International Patent Classification[7]: C09D 11/00, 11/02

(21) International Application Number: PCT/US00/20940

(22) International Filing Date: 1 August 2000 (01.08.2000)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
60/147,917 9 August 1999 (09.08.1999) US

(71) Applicant: CABOT CORPORATION [US/US]; 75 State Street, Boston, MA 02109-1806 (US).

(72) Inventor: BATES, Jodi, A.; 16 Eldorado Road, Chelmsford, MA 01824 (US).

(74) Agent: LANDO, Michelle, B.; Cabot Corporation, 157 Concord Road, P.O. Box 7001, Billerica, MA 01821-7001 (US).

(81) Designated States *(national)*: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CR, CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZW.

(84) Designated States *(regional)*: ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Published:
— *With international search report.*

For two-letter codes and other abbreviations, refer to the "Guidance Noies on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

WO 01/10963 A1

(54) Title: INK COMPOSITIONS HAVING MODIFIED PIGMENTS WITH HIGH OR LOW TREATMENT LEVELS

(57) Abstract: Ink compositions having modified pigments with high or low treatment levels are described. Ink compositions having modified pigments with high treatment levels comprise 1) at least one liquid vehicle and 2) at least one modified pigment, wherein the modified pigment comprises at least one pigment having attached at least one organic group substituted with at least one anionic group, at least one anionizable group, or a mixture thereof, wherein the organic group is present at a treatment level of from about 4.5 to about 7.5 micromoles/m^2 of the pigment used based on nitrogen surface area of the pigment. Ink compositions having modified pigments with low treatment levels comprise 1) at least one liquid vehicle and 2) at least one modified pigment, wherein the modified pigment comprises at least one pigment having attached at least one organic group substituted with at least one cationic group, at least one cationizable group, or a mixture thereof, wherein the organic group is present at a treatment level of from about 1 to about 4 micromoles/m^2 of the pigment used based on nitrogen surface area of the pigment. The present invention further relates to methods for improving intercolor bleed properties of an ink, by using the above-described components in an ink.

TITLE

INK COMPOSITIONS HAVING MODIFIED PIGMENTS WITH HIGH OR LOW TREATMENT LEVELS

BACKGROUND OF THE INVENTION

1. Field of the Invention.

The present invention relates to ink compositions having modified pigments with high or low levels of organic treatment. The ink compositions exhibit improved intercolor bleed properties and are suitable in inkjet printing inks and in inks incorporating such modified pigments.

2. Description of the Related Art.

Inkjet printing is a non-impact process wherein droplets of ink are produced and deposited on a substrate such as paper, transparent film, polymer sheet, or textile material in response to an electronic signal. Inkjet printing systems are typically classified by two known types: continuous stream or drop on demand. Thermal or bubble jet drop-on-demand inkjet printers are useful outputs for personal computers in the office and in the home.

A common problem associated with certain inkjet printing processes is that color can "bleed" between different color regions of the printed substrate. "Bleed" is defined as the migration of one ink color into a region of another ink color, particularly when black ink moves into a region of any other color. In general, an inkjet printer is capable of printing with colored ink such as magenta, cyan, yellow, and black ink. When the two colors are printed side by side, there is a tendency for the colors to bleed into one another. When color bleed occurs, the boundary between adjacent color regions becomes indistinct or blurred, resulting in a low resolution printed image. To produce

high resolution colored images using inkjet printing processes, there is a need for ink compositions that exhibit low or improved intercolor bleed.

Ink compositions that are useful in imaging applications, such as inkjet ink printing systems, are well known and generally contain water-soluble dyes. Although dye based inks are suitable for their intended purpose, dyes have several disadvantages when used in inkjet inks. For instance, dyes, being water-soluble in a water/organic mixture may dissolve and run when exposed to moisture or water. Dye images may further smear or rub off on contact with felt pen markers or upon being rubbed or touched by fingers. Dyes also exhibit poor stability when exposed to visible, ultraviolet light, or sunlight. In addition, dyes can have a problem with intercolor bleed.

Because of the limitations of the water-soluble dye approach, researchers have worked with pigment based inks. However, while pigments are beginning to receive a wide degree of acceptance in inkjet ink systems, for example, there are still problems associated with the performance and reliability of the composition, i.e., print properties, stability, and the like.

As a result, a need remains for improved ink compositions, especially for use in inkjet printing processes, which overcomes the problems that are typically associated with current dye based and pigment systems. In addition, there is a need for improved ink compositions, which provide improved intercolor bleed properties and generate images having good print properties.

SUMMARY OF THE INVENTION

The present invention relates to ink compositions having modified pigments with high or low treatment levels. The ink compositions contain modified pigments with high treatment levels and at least one liquid vehicle. The modified pigment is a pigment having attached at least one organic group. The organic group is substituted with at least one anionic group, at least one anionizable group, or a mixture thereof. The organic group is present at a treatment level of from about 4.5 to about 7.5 micromoles/m^2 of the pigment used based on nitrogen surface area of the pigment.

The present invention also relates to ink compositions having modified pigments with low treatment levels. Ink compositions having modified pigments with low treatment levels comprise 1) at least one liquid vehicle and 2) at least one modified pigment. The modified pigment is a pigment having attached at least one organic group. The organic group is substituted with at least one cationic group, at least one cationizable group, or a mixture thereof. The organic group is present at a treatment level of from about 1.0 to about 4.0 micromoles\m^2 of the pigment used based on nitrogen surface area of the pigment.

The pigment can be a carbon product, a colored pigment other than a carbon product, a multi-phase aggregate comprising at least one carbon phase and at least one silicon-containing species phase, a multi-phase aggregate containing at least one carbon phase and at least one metal-containing species phase, a partially silica coated carbon black, or mixtures thereof.

The organic group can comprise at least one aromatic group or C_1-C_{20} alkyl group, or mixtures or combinations thereof. The liquid vehicle is preferably aqueous.

The present invention further relates to methods for improving intercolor bleed properties of an ink, by introducing the above-described modified pigments to the ink. The present invention also relates to inkjet ink compositions comprising the above-described ink compositions.

Additional features and advantages of the present invention are set forth in the detailed description and examples that follow, or may be learned by practice of the present invention. These aspects and other advantages will be realized and obtained by the various embodiments described and pointed out in the claims.

DETAILED DESCRIPTION OF THE PRESENT INVENTION

The present invention relates to ink compositions having modified pigments with high or low treatment levels. Ink compositions having modified pigments with high treatment levels contain 1) at least one liquid vehicle and 2) at least one modified pigment. The modified pigment is a pigment having attached at least one organic group. The organic group is substituted with at least one anionic group, at least one anionizable group, or a mixture thereof. An anionizable group means an ionizable group capable of forming an anion. The organic group is present at a treatment level of from about 4.5 to about 7.5 micromoles/m^2 of the pigment used based on nitrogen surface area of the pigment. Preferably, the organic group is present at a treatment level of from about 5.0 to about 7.0 micromoles/m^2 of the pigment used based on nitrogen surface area of the pigment.

The pigment, as used herein, can be any pigment that can be modified with the attachment of at least one organic group. Examples include, but are not limited to, a carbon product, a colored pigment other than a carbon product, a multi-phase aggregate comprising at least one carbon phase and at least one silicon-containing species phase, a multi-phase aggregate containing at least one carbon phase and at least one metal-containing species phase, a partially silica coated carbon black, or mixtures thereof.

Carbon, as used herein, may be of the crystalline or amorphous type. Examples include, but are not limited to, graphite, carbon black, carbon fiber, vitreous carbon, activated charcoal, or activated carbon. Finely divided forms of the above are preferred. Also, it is possible to utilize mixtures of different colored pigments, mixtures of different carbon blacks, or combinations thereof.

Colored pigments, as used herein, include but are not limited to, colored pigments such as blue, brown, cyan, green, violet, magenta, red, yellow, as well as mixtures thereof. Suitable classes of color pigments include, for example, anthraquinones, phthalocyanine blues, phthalocyanine greens, diazos, monoazos, pyranthrones, perylenes, heterocyclic yellows, quinacridones, and (thio)indigoids. Such pigments are commercially available in either powder or press cake form from a

number of sources including, BASF Corporation, Engelhard Corporation and Sun Chemical Corporation. Examples of other suitable colored pigments are described in the *Colour Index*, 3rd edition (The Society of Dyers and Colourists, 1982). Representative examples of black pigments include various carbon blacks (Pigment Black 7) such as channel blacks, furnace blacks and lamp blacks, and include, for example, carbon blacks sold under the Regal®, Black Pearls®, Elftex®, Monarch®, Mogul®, and Vulcan® trademarks available from Cabot Corporation (such as Black Pearls® 2000, Black Pearls® 1400, Black Pearls® 1300, Black Pearls® 1100, Black Pearls® 1000, Black Pearls® 900, Black Pearls® 880, Black Pearls® 800, Black Pearls® 700, Black Pearls® L, Elftex® 8, Monarch® 1400, Monarch® 1300, Monarch® 1100, Monarch® 1000, Monarch® 900, Monarch® 880, Monarch® 800, Monarch® 700, Mogul® L, Regal® 330, Regal® 400, Vulcan® P). Other suitable carbon blacks include, but are not limited to, Printex 40, Printex 80, Printex 300, Printex L, Printex U, Printex V, Special Black 4, Special Black 5, FW200, (the foregoing available from Degussa Corporation), Raven 780, Raven 890, Raven 1020, Raven 1040, Raven 1255, Raven 1500, Raven 5000, Raven 5250 (the foregoing available from Columbian Chemical Corporation) and MA100 and MA440 available from Mitsubishi Chemical Corporation.

The multi-phase aggregate containing at least one carbon phase and at least one silicon-containing species phase can also be considered a silicon-treated carbon black aggregate and the multi-phase aggregate containing at least one carbon phase and at least one metal-containing species phase can also be considered to be metal-treated carbon black aggregate as long as one realizes that in either case, the silicon-containing species and/or metal-containing species are a phase of the aggregate just like the carbon phase.

The metal-treated carbon blacks are aggregates containing at least one carbon phase and at least one metal-containing species phase. The metal-containing species include compounds containing aluminum, zinc, magnesium, calcium, titanium, vanadium, cobalt, nickel, zirconium, tin, antimony, chromium, neodymium, lead, tellurium, barium, cesium, iron, and molybdenum. Preferably, the metal-containing

species phase is an aluminum- or zinc-containing species phase. The metal-containing species phase(s) can be distributed through at least a portion of the aggregate and is an intrinsic part of the aggregate.

The details of making the multi-phase aggregates are explained in U.S. Patent Nos. 5,904,762, 5,877,238, 5,869,550, 5,749,950, 6,017,980, and 6,057,387 and in PCT Publication No. WO 96/37547, the disclosures of which are herein incorporated in their entireties by reference.

A partially silica coated carbon product can also be used as the pigment, such as that described in PCT Publication No. WO 96/37547, published November 28, 1996, which is hereby incorporated in its entirety herein by reference.

The pigment can have any particle size suitable for use in inks and/or coatings. A higher surface area is preferred, such as about 200 m^2/g or higher, and a low DBP is also preferred, such as from about 60 to about 100.

The modified pigment is a pigment having attached at least one organic group. The organic group can be at least one aromatic group and/or C_1-C_{20} alkyl group and can be directly attached to the pigment. The aromatic group includes, but is not limited to, unsaturated cyclic hydrocarbons containing one or more rings. The aromatic group may be substituted or unsubstituted. Aromatic groups include, but are not limited to, aryl groups (for example, phenyl, naphthyl, anthracenyl, and the like), and heteroaryl groups (imidazolyl, pyrazolyl, pyridinyl, thienyl, thiazolyl, furyl, triazinyl, indolyl, and the like).

In another aspect of the invention, the organic group can also be an olefin group, a styrenic group, an acrylate group, an amide group, an ester group, or mixtures thereof.

Further, the organic group can be a polymeric group, such as a polyolefin group, a polystyrenic group, a polyamide group, a polyester group, or mixtures thereof. The organic group can also be an alkylene oxide.

Examples of organic groups are described in U.S. Patent Nos. 5,895,522, 5,885,335, 5,803,959, 5,851,280, 5,837,045, 5,672,198, 5,571,311, 5,630,868, 5,707,432, 5,554,739, 5,698,016, 5,713,988, and 5,803,959, in PCT Publication Nos.

WO 96/18688, WO 97/47697, WO 97/47699, and WO 99/51690, as well as in U.S. Patent Application No. 08/990,715, all incorporated herein in their entireties by reference.

The liquid vehicle is preferably aqueous. Examples include, but are not limited to, water, water-soluble organic solvents, other organic solvents, and the like.

Anionizable functional groups forming anions include, for example, acidic groups or salts of acidic groups. The organic group, therefore, can include groups derived from organic acids. Preferably, when the organic group contains an ionizable group forming an anion, the organic group has a) an aromatic group or C_1-C_{20} alkyl group and b) at least one acidic group having a pKa of less than 11, or at least one salt of a acidic group having a pKa of less than 11, or a mixture of at least one acidic group having a pKa of less than 11 and at least one salt of an acidic group having a pKa of less than 11. The pKa of the acidic group refers to the pKa of the organic group as a whole, not just the acidic substituent. More preferably, the pKa is less than 10 and most preferably less than 9. The aromatic group may be further substituted or unsubstituted, for example, with alkyl groups. More preferably, the organic group is a phenyl or a naphthyl group and the acidic group is a sulfonic acid group, a sulfuric acid group, a phosphonic acid group, or a carboxylic acid group. The naphthyl group may be mono-substituted with an acidic group on either ring. The naphthyl group may also be substituted with two or more acidic groups, with the acidic groups on the same or different rings. Examples of ionic or ionizable groups include -COOH, -SO_3H and -PO_3H_2, -SO_2NHCOR, and their salts, for example, -COONa, -COOK, -$COO^-NR_4^+$, -SO_3Na, -$SO_3^-NR_4^+$, and PO_3Na_2, where R is a saturated or unsaturated alkyl or phenyl group. Particularly preferred ionic or ionizable substituents are -COOH and -SO_3H and their sodium and potassium salts.

The modified pigment may be prepared preferably by reacting a pigment, such as carbon black, with a diazonium salt in a liquid reaction medium to attach at least one organic group to the surface of the pigment. The diazonium salt may contain the organic group to be attached to the pigment. A diazonium salt is an organic compound having one or more diazonium groups. Preferred reaction media include water, any

medium containing water, and any medium containing alcohol. Water is the most preferred medium. Examples of modified carbon products, wherein the carbon is carbon black, and various preferred methods for their preparation are described in U.S. Patent No. 5,851,280 entitled "Reaction of Carbon Black with Diazonium Salts, Resulting Carbon Black," incorporated herein by reference in its entirety. Examples of modified carbon products, wherein the carbon is not carbon black, and various preferred methods for their preparation are described in U.S. Patent No. 5,554,739, 5,837,045, WO 96/18696 and WO 96/18688, incorporated herein by reference in their entirety. The pigments other than carbon products can be prepared in a similar manner.

The amount of organic group attached to the pigment is an important factor for purposes of the subsequent use of the modified pigment and such applications as inkjet ink compositions, coating formulations, and ink systems. In particular, for ink compositions containing the anionic or anionizable groups in the pigment, the treatment levels should be of a high level especially if excellent resistance to intercolor bleed is desired. In other words, the treatment levels of organic groups may be from about 4.5 to about 7.5 micromoles/m^2 of the pigment used, more preferably from about 5.0 to about 7.0 micromoles/m^2 of the pigment used, based on nitrogen surface area of the pigment. The treatment level refers to the amount of organic group that is reacted in the presence of the pigment. The amount attached will typically be a percentage of this level depending on such factors as pigment, type of organic group and processing conditions. The optimum treatment level is a balance between properties such as optical density, waterfastness, and intercolor bleed. Treatment levels that provide higher optical density and better waterfastness tend to compromise intercolor bleed. Thus, there is a need to find the right balance of these properties which is accomplished by the present invention.

The results obtained by the present invention are surprising and unexpected since high treatment levels are suitable for use in inks when the organic group is anionic or anionizable, but the same is not true for inks containing cationic or cationizable groups on the pigment.

In general, the ink compositions of the present invention may be prepared utilizing conventional techniques know to those skilled in the art, such as combining or mixing the desired components in a suitable medium. Typically, the ink compositions are aqueous systems and include therein a significant amount of water, preferably deionized or distilled water. For example, the amount of water or similar medium is generally present in an amount ranging from about 60% to about 95%, preferably from about 75% to about 90%, based on the weight of the ink composition. Suitable additives are generally incorporated into the ink compositions to impart a number of desired properties while maintaining the stability of the compositions. Such additives are well known in the art and include humectants, biocides, binders, drying accelerators, penetrants, surfactants, and the like. For example, a humectant may be added to reduce the rate of evaporation of water in the ink to minimize print head nozzle clogging. If the ink begins to dry out, the humectant concentration increases and evaporation is decreased further. Humectants may also affect other properties of the ink and prints made therefrom, such as viscosity, pH, surface tension, optical density, and print quality. Such humectants typically include ethylene glycol, propylene glycol, diethylene glycols, glycerine, dipropylene glycols, polyethylene glycols, polypropylene glycols, alkane diols, amides, ethers, carboxylic acids, esters, alcohols, organsulfides, organosulfoxides, sulfones, alcohol derivatives, 2-pyrrolidone, ether derivatives, amino alcohols, and ketones. The amount of a particular additive will vary depending on a variety of factors including the molecular weight of the polymers, the viscosity, the amount added, as well as the nature of the polymers, the nature of any organic groups attached to the pigment, e.g., modified carbon black products.

The present invention also relates to a method for improving intercolor bleed properties of an ink, by introducing at least one modified pigment to the ink, wherein the modified pigment is described above using the treatment levels described earlier.

The present invention further relates to ink compositions having modified pigments with low treatment levels. Ink compositions having modified pigments with low treatment levels comprise 1) at least one liquid vehicle and 2) at least one modified pigment. The modified pigment is a pigment having attached at least one organic

group. The organic group is substituted with at least one cationic group, at least one cationizable group, or a mixture thereof. The organic group is present at a treatment level of from about 1.0 to about 4.0 micromoles/m^2 of the pigment used based on nitrogen surface area of the pigment. Preferably, the organic group is present at a treatment level of from about 2 to about 3 micromoles/m^2 of the pigment used based on nitrogen surface area of the pigment. As with the anionic or anionizable organic groups described above, the treatment level again refers to the amount of organic group that is reacted in the presence of the pigment. Similarly, the amount attached will typically be a percentage of this level depending on such factors as pigment, type of organic group and processing conditions. In addition, the optimum treatment level is a balance between properties such as optical density, waterfastness and intercolor bleed.

For purposes of this embodiment, the amount of organic group attached to the pigment can be important factor for purposes of the subsequent use of the modified pigment and such applications as inkjet ink compositions, coating formulations, and ink systems. In particular, for cationic ink compositions the levels should be of a low level as described above.

The results obtained by the present invention are surprising and unexpected since low treatment levels are suitable for inks containing modified pigments with cationic groups, but not inks containing modified pigments with anionic groups. Thus, in certain situations, attaching low levels of organic groups to modified pigments results in better properties.

A cationizable group is an ionizable group that is capable of forming a cation in the medium of use. Amines represent examples of cationizable groups that form cations and cationic groups and can be attached to the same organic groups as discussed above for the anionizable groups that form anions. For example, amines may be protonated to form ammonium groups in acidic media. Preferably, an organic group having an amine substituent, wherein the amine substituent has a pKb of less than 5.

Quaternary ammonium groups (-NR_3^+) and quaternary phosphonium groups (-PR_3^+) also represent examples of cationic groups and can be attached to the same organic groups as discussed above for anionizable groups that form anions. Preferably,

the organic group contains an aromatic group such as phenyl or naphthyl group and a quaternary ammonium or a quaternary phosphonium group. Quaternized cyclic amines, and quaternized aromatic amines, can also be used as the organic group.

The inkjet ink compositions have improved intercolor bleed properties compared to dye based inkjet inks. For instance, the inkjet ink compositions of the present invention can have an average intercolor bleed of good to excellent.

In general, the ink compositions of the present invention may be prepared utilizing the same conventional techniques as described earlier. These techniques include, but are not limited to, combining or mixing the desired components in a suitable medium.

The present invention further relates to a method for improving intercolor bleed properties of an ink, comprising introducing 1) at least one liquid vehicle and 2) at least one modified pigment to an ink, wherein the modified pigment comprises at least one pigment having attached at least one organic group substituted with at least one cationic group, at least one cationizable group, or a mixture thereof, wherein said organic group is present at treatment levels described earlier.

The modified pigments of the present invention are also useful in aqueous ink and coating formulations. Aqueous includes mixtures of water and other water-miscible or - dispersible substances, such as an alcohol. Thus, the invention provides an aqueous ink composition comprising water and a modified pigment according to the invention. Other known aqueous ink additives may be incorporated into the aqueous ink formulation. As stated previously, an ink may consist of the various components described above. Various aqueous ink compositions are also disclosed, for example, in United States Patent Nos. 2,833,736; 3,607,813; 4,104,833; 4,308,061; 4,770,706; and 5,026,755, all incorporated herein by reference.

As stated earlier, modified pigments of the present invention are particularly useful in inkjet ink formulations. The additives and formulations described in U.S. Patent Nos. 5,571,311 and 5,630,868 can be used herein with the modified pigments of the present invention.

The modified pigments of the present invention, either as a predispersion or as a solid, can be incorporated into an aqueous ink formulation using standard techniques.

Flexographic inks represent a group of ink compositions. Flexographic inks generally include a colorant, a binder, and a non-aqueous or aqueous solvent. The modified pigments of the invention may be useful as flexographic ink colorants. The modified pigments of the invention may be used in aqueous news inks. For example, an aqueous news ink composition may comprise water, the modified pigments of the invention, a resin and conventional additives such as antifoam additives or a surfactant.

As stated earlier, the modified pigments of this invention may also be used in aqueous coating compositions such as paints or finishes. Thus, an embodiment of the invention is an aqueous coating composition comprising water, resin and at least one modified pigment according to the invention. Other known aqueous coating additives may be incorporated into the aqueous coating composition. See, for example, McGraw-Hill Encyclopedia of Science & Technology, 5th Ed. (McGraw-Hill, 1982), incorporated herein by reference. See also United States Patent Nos. 5,051,464, 5,319,044, 5,204,404, 5,051,464, 4,692,481, 5,356,973, 5,314,945, 5,266,406, and 5,266,361, all incorporated herein by reference. The aqueous compositions of the present invention may also comprise additional other coloring pigments (e.g. TiO_2, phthalo blue and the like), clays, talc, silicas, and carbonates. The modified pigments of the invention, either as a predispersion or as a solid, can be incorporated into an aqueous coating composition using standard techniques.

Also, the modified pigments of the present invention can be used in ink jet inks where the ink formulation may be based on solvents, aqueous media, or an aqueous emulsion.

To control intercolor bleed and optimize pigment and ink performance, the proper level and type of treatment needs to be selected. In the examples given, a relatively higher level of anionically modified pigment or a relatively lower level of cationically modified pigment achieved the desired level of performance. The following examples are intended to further illustrate, not to limit, the claimed invention.

EXAMPLES

Example 1

Inkjet inks were made using surface modified carbon blacks that are ionically stabilized in water. The group attached to the carbon black surface was a carboxylic acid salt with an ammonium counterion. These blacks were prepared following a procedure similar to that described in U.S. Patent No. 5,630,868. The formula consisted of 3% pigment solids, 7.5% ethylene glycol, 7.5% glycerol, 4% isopropanol, and the remainder deionized water, all by wt% of formulation. The inks were then filled in to a cleaned inkjet cartridge (BJC-21) and printed on NSK paper using a Canon BJC 4200 printer. The pattern used for the print testing contained on the left side 3 boxes of black text at varying font sizes in each of the three primary colors, cyan, magenta, and yellow and on the right 3 boxes of colored text in black boxes. These prints were visually assessed for intercolor bleed using a 10X magnification loop. The morphology of the carbon blacks used in the modification, the treatment level, and the indirect measure of modification (as measured by counterion concentration) are included in Table 1.

TABLE 1

Sample Number	Carbon Black Morphology		Treatment Level	Counterion
	Nitrogen Surface Area (m^2/g)	Dibutyl Phthalate Absorption (cc/100g)	micromol/m^2	ppm
1 A	210	74	4.0	4996
1 B	210	74	6.4	8258
2 A	200	95	4.0	5129
2 B	200	95	5.2	6585
2 C	200	95	6.4	6907
3 A	220	112	4.0	6369
3 B	220	112	6.4	7233
4 A	240	65	4.0	6610
4 B	240	65	6.6	9106

The results (see Table 2) indicate that the treatment level of the surface modified pigments impacts the resultant intercolor bleed properties of an ink when printed. It can be concluded from these results that a higher treatment level positively influences the intercolor bleed properties of an ink formulated with an anionically stabilized surface modified pigment dispersion. A lesser effect was also observed where the morphology of the surface modified carbon black contributes to intercolor bleed. As the surface area increases and the dibutyl phthalate absorption decreases a slight improvement in the ink's intercolor bleed properties were noted. However, it was noted that with an improvement in intercolor bleed, a corresponding decline in waterfastness and to a lesser extent optical density were observed in all cases. Waterfastness and optical density results were within acceptable limits and these formulas should be considered viable and useful.

TABLE 2

Sample Number	Average Particle Size (microns)	Optical Density	Waterfastness	Intercolor Bleed
1A	0.076	1.26	5 min	fair
1B	0.074	1.24	10 min	good
2A	0.096	1.37	5 min	fair
2B	0.108	1.34	5 min	good
2C	0.084	1.34	10 min	Good to very good
3A	0.101	1.43	10 min	fair
3B	0.094	1.35	1 hr	good
4A	0.066	1.21	5 min	fair
4B	0.065	1.20	> 1 hr	Very good

Example 2

Inkjet inks were made using surface modified furnace carbon blacks that were cationically stabilized in water. The group attached to the carbon black surface was a pyridinium quaternary amine salt with nitrate counterion. These blacks were prepared following a procedure similar to that described in U.S. Patent No. 5,630,868. The

formula consisted of 5% pigment solids, 7.0% glycerol, 5.0% diethylene glycol, 7% trimethanol propane and the remainder deionized water (all by wt% of formulation). The inks were then filled in to a cleaned inkjet cartridge (BJC-21) and printed on Xerox 4024 paper using a Canon BJC 4200 printer. The pattern used for the print testing contained on the left side 3 boxes of black text at varying font sizes in each of the three primary colors, cyan, magenta, and yellow and on the right 3 boxes of colored text in black boxes. These prints were visually assessed for intercolor bleed using a 10X magnification loop. The morphology of the carbon blacks used in the modification, the treatment levels, and the indirect measure of modification (as measured by counterion concentration) are included in Table 3.

TABLE 3

Sample Number	Carbon Black Morphology		Treatment Level	Counterion
	Nitrogen Surface Area (m^2/g)	Dibutyl Phthalate Absorption (cc/100g)	micromol/m^2	ppm
6A	200	117	2.2	14,392
6B	200	117	2.5	17,100
6C	200	117	3.0	21,953
6D	200	117	5.0	23,732
6E	200	117	7.5	27,997

These results indicate (see Table 4) that the treatment level of the surface modified pigments impact the resultant intercolor bleed properties of an ink when printed. It can be concluded from these results that a lower treatment level positively influences the intercolor bleed properties of an ink formulated with a cationically surface modified pigment dispersion. From these results, an optimum level of 3.0 micromol/m^2 was noted. However, at the optimum treatment level for intercolor bleed, a corresponding decline in waterfastness and optical density were observed when compared to the lower treatment levels. Waterfastness and optical density results were within acceptable limits for the optimal intercolor bleed and should be considered viable and useful.

TABLE 4

Sample Number	Average Particle Size (microns)	Optical Density	Waterfastness	Intercolor Bleed
6A	0.135	1.49	5 min	fair
6B	0.139	1.47	5 min	fair
6C	0.235	1.40	1 hr	good
6D	0.139	1.35	> 1 hr	poor
6E	0.144	1.41	> 1 hr	poor

Example 3

Inkjet inks were made using surface modified channel-like carbon blacks that were ionically stabilized in water. The volatile content of the carbon black used in this example was significantly higher than the carbon blacks outlined in the previous examples (14.5% vs. <1.0%). The group attached to the carbon black surface was a carboxylic acid salt with a sodium counterion. These blacks were prepared following a procedure similar to that described in U.S. Patent No. 5,360,868. The formula consisted of 4% pigment solids, 10.0% 1,4-butanediol, 10.0% 2-pyrrolidinone, 4% isopropanol and the remainder deionized water, all by weight of the formulation. The inks were then filled in to a cleaned inkjet cartridge (12A1970) and printed on Hammermill DP Fore paper using a Lexmark Color Jetprinter Series 7000 printer. The pattern used for the print testing contained small boxes of black text in each of the three primary colors, cyan, magenta, and yellow and small boxes of colored text in black boxes. These prints were visually assessed for intercolor bleed using a 10X magnification loop. The morphology of the carbon blacks used in the modification, the treatment levels, and the indirect measure of modification (as measured by counterion concentration) are included in Table 5.

TABLE 5

Sample Number	Carbon Black Morphology		Treatment Level	Counterion
	Nitrogen Surface Area (m^2/g)	Dibutyl Phthalate Absorption (cc/100g)	micromol/m^2	ppm
7A	180	110	2.7	7,301
7B	180	110	4.0	11,871
7C	180	110	7.5	11,250

These results (see Table 6) indicate that the treatment level of the surface modified pigments impact the resultant intercolor bleed properties of an ink when printed. It can be concluded from these results that a higher treatment level positively influences the intercolor bleed properties of an ink formulated with an anionically stabilized, channel-like surface modified carbon black pigment dispersion. However, it was noted that with an improvement in intercolor bleed, a corresponding decline in waterfastness was observed in all cases. Waterfastness results were within acceptable limits and these formulas should be considered viable and useful. In comparing sample 7B and 7C, it was also observed that with a given carbon product, it was possible to maximize the level of attached groups.

TABLE 6

Sample Number	Average Particle Size (microns)	Optical Density	Waterfastness	Intercolor Bleed
7A	0.159	1.46	5 min	fair
7B	0.154	1.46	10 min	good
7C	0.155	1.47	1 hr	good

Other embodiments of the present invention will be apparent to those skilled in the art from consideration of the specification, examples and practice of the invention disclosed herein. It is intended that the specification be considered as exemplary only, with a true scope and spirit of the invention being indicated by the following claims.

What we claim is:

CLAIMS

1. An ink composition comprising 1) at least one liquid vehicle and 2) at least one modified pigment, wherein said modified pigment comprises at least one pigment having attached at least one organic group substituted with at least one anionic group, at least one anionizable group, or a mixture thereof, wherein said organic group is present at a treatment level of from about 4.5 to about 7.5 micromoles/m^2 of the pigment used based on nitrogen surface area of the pigment.

2. The ink composition of claim 1, wherein the organic group is present at a treatment level of from about 5.0 to about 7.0 micromoles/m^2 of the pigment used based on nitrogen surface area of the pigment.

3. The ink composition of claim 2, wherein the organic group is present at a treatment level of from about 5.5 to about 6.5 micromoles/m^2 of the pigment used based on nitrogen surface area of the pigment.

4. An ink composition comprising 1) at least one liquid vehicle and 2) at least one modified pigment, wherein said modified pigment comprises at least one pigment having attached at least one organic group substituted with at least one cationic group, at least one cationizable group, or a mixture thereof, wherein said organic group is present at a treatment level of from about 1 to about 4 micromoles/m^2 of the pigment used based on nitrogen surface area of the pigment.

5. The ink composition of claim 4, wherein the organic group is present at a treatment level of from about 2 to about 3 micromoles/m^2 of the pigment used based on nitrogen surface area of the pigment.

6. The ink composition of claims 1-5, wherein said pigment is a carbon product, a colored pigment other than a carbon product, a multi-phase aggregate comprising at

least one carbon phase and at least one silicon-containing species phase, a multi-phase aggregate comprising at least one carbon phase and at least one metal-containing species phase, a partially silica coated carbon black, or mixtures thereof.

7. The ink composition of claims 1-5, wherein said organic group comprises at least one aromatic group or C_1-C_{20} alkyl group.

8. The ink composition of claim 7, wherein said at least one aromatic group or C_1-C_{20} alkyl group is directly attached to the pigment.

9. The ink composition of claims 1-5, wherein said organic group is a polymeric group.

10. The ink composition of claims 1-5, wherein said organic group is an alkylene oxide.

11. The ink composition of claims 1-5, wherein said carbon product is carbon black.

12. The ink composition of claims 1-5, wherein said pigment is a colored pigment.

13. The ink composition of claims 1-5, wherein the liquid vehicle is aqueous.

14. The ink composition of claims 1-5, wherein said ink composition is an inkjet ink composition.

15. A method for improving intercolor bleed properties of an ink, comprising introducing 1) at least one liquid vehicle and 2) at least one modified pigment to an ink formulation, wherein said modified pigment comprises at least one pigment having attached at least one organic group substituted with at least one anionic group, at least one anionizable group, or a mixture thereof, wherein said organic group is

present at a treatment level of from about 4.5 to about 7.5 micromoles/m^2 of the pigment used based on nitrogen surface area of the pigment.

16. The method of claim 15, wherein the organic group is present at a treatment level of from about 5.0 to about 7.0 micromoles/m^2 of the pigment used based on nitrogen surface area of the pigment.

17. The method of claim 16, wherein the organic group is present at a treatment level of from about 5.5 to about 6.5 micromoles/m^2 of the pigment used based on nitrogen surface area of the pigment.

18. A method for improving intercolor bleed properties of an ink, comprising introducing 1) at least one liquid vehicle and 2) at least one modified pigment to said ink, wherein said modified pigment comprises at least one pigment having attached at least one organic group substituted with at least one cationic group, at least one cationizable group, or a mixture thereof, wherein said organic group is present at a treatment level of from about 1 to about 4 micromoles/m^2 of the pigment used based on nitrogen surface area of the pigment.

19. The method of claim 18, wherein the organic group is present at a treatment level of from about 2 to about 3 micromoles/m^2 of the pigment used based on nitrogen surface area of the pigment.

20. The method of claims 15-19, wherein said pigment is a carbon product, a colored pigment other than a carbon product, a multi-phase aggregate comprising at least one carbon phase and at least one silicon-containing species phase, a multi-phase aggregate comprising at least one carbon phase and at least one metal-containing species phase, a partially silica coated carbon black, or mixtures thereof.

21. The method of claims 15-19, wherein said organic group comprises at least one aromatic group or C_1-C_{20} alkyl group.

22. The method of claim 21, wherein said at least one aromatic group or C_1-C_{20} alkyl group is directly attached to the pigment.

23. The method of claims 15-19, wherein said organic group is a polymeric group.

24. The method of claims 15-19, wherein said organic group is an alkylene oxide.

25. The method of claims 15-19, wherein said carbon product is carbon black.

26. The method of claims 15-19, wherein said pigment is a colored pigment.

27. The method of claims 15-19, wherein the liquid vehicle is aqueous.

28. The method of claims 15-19, wherein said ink formulation is an inkjet ink formulation.

INTERNATIONAL SEARCH REPORT

Interr nal Application No
PCT/US 00/20940

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C09D11/00 C09D11/02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C09D C09C C09B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 99 23174 A (CABOT CORP) 14 May 1999 (1999-05-14) page 7, line 5 -page 12, line 3; claims 1-80	1-28
A	EP 0 475 075 A (XEROX CORP) 18 March 1992 (1992-03-18) page 5, line 7-16 page 6, line 7-21	4,6,9, 11,13,14
A	GB 2 323 600 A (HEWLETT PACKARD CO) 30 September 1998 (1998-09-30) page 5, line 21-27 page 7, line 23 -page 9, line 27	1,4,6, 11-14

-/--

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
24 October 2000	03/11/2000

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Miller, A

1

Form PCT/ISA/210 (second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

Inter: nal Application No
PCT/US 00/20940

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 97 48769 A (CABOT CORP) 24 December 1997 (1997-12-24) page 5, line 4 -page 6, line 16 & US 5 837 045 A (JAMES A. BELMONT) 17 November 1998 (1998-11-17) cited in the application	1-28
A	WO 99 07794 A (CABOT CORP) 18 February 1999 (1999-02-18) page 3, line 15 -page 4, line 8 & US 5 895 522 A (JAMES A. BELMONT) 20 April 1999 (1999-04-20) cited in the application	1-28

Form PCT/ISA/210 (continuation of second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

Information on patent family members

Intern nal Application No
PCT/US 00/20940

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9923174 A	14-05-1999	US 6068688 A	30-05-2000
		AU 1283099 A	24-05-1999
		EP 1027388 A	16-08-2000
EP 0475075 A	18-03-1992	US 5281261 A	25-01-1994
		CA 2046571 A,C	01-03-1992
		DE 69114962 D	11-01-1996
		DE 69114962 T	18-04-1996
		JP 3048692 B	05-06-2000
		JP 4234467 A	24-08-1992
GB 2323600 A	30-09-1998	US 5886065 A	23-03-1999
		DE 19748916 A	01-10-1998
		JP 10265727 A	06-10-1998
		US 6034153 A	07-03-2000
		US 5891934 A	06-04-1999
WO 9748769 A	24-12-1997	US 5837045 A	17-11-1998
		AU 3232897 A	07-01-1998
		EP 0906371 A	07-04-1999
WO 9907794 A	18-02-1999	US 5895522 A	20-04-1999
		AU 8698598 A	01-03-1999
		EP 1007595 A	14-06-2000
		US 5968243 A	19-10-1999